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First-principles study of interstitial diffusion of oxygen in nickel chromium binary alloy

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The first-principles calculations of the diffusion processes of oxygen in pure Ni and Ni-Cr binary alloy are conducted to understand the oxidation behavior of nickel base alloys. The cohesive energy, insertion energy of atomic oxygen, and vacancy formation energy in nickel are calculated and compared with experimental data. The activation energies of oxygen are also calculated. The results show agreement with previous work for the oxygen diffusion in pure nickel. However, the calculated activation energy for the diffusion of oxygen in Ni-Cr binary alloy showed lower values than that in nickel because of the limitations of the current calculation model. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3696079]

Nickel base alloys have been widely used as structural materials in various engineering systems because they have excellent mechanical strength and creep resistance, and high corrosion and oxidation resistance in high temperature environment. However, these materials have shown to suffer from environment-assisted cracking (EAC) in high temperature condition, which is generally considered as a cracking phenomenon caused by a combined process of corrosion/oxidation and strain on a metal due to residual or applied stressed within the susceptible environment.[1]

Many experimental studies have been performed to explain the governing mechanism of EAC of nickel base alloys and have drawn several different arguments with some possible ways to reveal the process and prevent it, such as slip dissolution/oxidation,[2] corrosion-enhanced plasticity,[3] internal oxidation,[4,5] and creep.[6] However, there is no general theory to explain the EAC of nickel base alloys, because the EAC is a very complex phenomena affected by many parameters and the corrosion/oxidation process takes place slowly in tiny localized areas.

Meanwhile, according to the increase in the computer calculation capability, atomistic modeling and simulation methods have been receiving much attention as an alternative way to evaluate the mechanical properties and thermodynamic properties of metals and alloys.[7] Very recently, modeling and simulation studies have started to be applied to understand the fundamental mechanism of nickel and nickel base alloy corrosion and oxidation processes in high temperature condition. In order to evaluate the damage process by corrosion and oxidation in structural alloys, it is necessary to combine molecular dynamics simulation and first principles calculation. First-principles calculation can be used to get interatomic potential between interested atoms and oxygen, which can be essential parameters in molecular dynamics simulation including vacancy migration energy, diffusion activation energy, bulk modulus and so on.

For pure nickel, Garruchet *et al.*[8] evaluated the diffusion of oxygen in nickel by the variable charge molecular dynamics, and Young *et al.*[9] calculated the diffusion coefficient of hydrogen and the activation energy of oxygen of diffusion in nickel by using the first-principles method and also Megchiche *et al.*[10] calculated the diffusion of oxygen in nickel using the first-principles calculation. In addition, the effect of thermal expansion on the diffusion process was studied by varying the lattice expansion that was concerned with varying the lattice constant by Finnis *et al.*[11] and Mishin *et al.*[12] They explored some properties in oxidation of bimetal such as NiAl. They evaluated the diffusion mechanisms in NiAl by embedded-atom and first-principles calculations. They focused on the diffusion of nickel atom in NiAl to see the effect of defect complex. The self-diffusion coefficient of nickel in NiAl was evaluated with the calculation of activation energy and vacancy jump frequency. The computational results have been compared with the experimental data, and the results have shown good agreement.

Since most of previous studies have focused on the diffusion of oxygen in pure Ni or nickel in NiAl, however, it needs to be extended to Ni-Cr binary system or Ni-Cr-Fe ternary system in order to understand the corrosion/oxidation behavior as well as the mechanism of EAC of nickel base structural alloys.

Therefore, the aim of this study is to understand the corrosion/oxidation behavior of nickel base alloys through the simulation of the diffusion processes of oxygen in pure Ni as well as Ni-Cr binary alloy. In detail, to check the accuracy of computational model and calculation, some basic parameters were calculated such as cohesive energy of Ni, insertion energy of oxygen in pure Ni, and vacancy formation energy. And, the activation energy of the diffusion of oxygen in pure Ni and Ni-Cr binary alloy were also calculated.

In this study, the first-principles calculation, which solves the Shrödinger equation with no experimental data, was used as a computational method. The calculations were performed by the Vinena first-principle simulation package (VSAP) developed at the Institute für Materialphysik of the Universität Wien.[13] The total energies, forces, and energy profiles are calculated using density function theory (DFT) (Ref. 14) with spin-polarization taken into account, all calculations were performed with the generalized gradient

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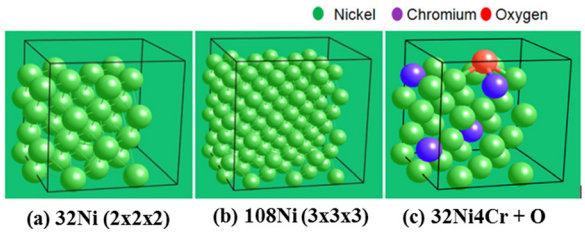

FIG. 1. (Color online) Atomic structure of supercells used in this study.

approximation (GGA) (Ref. 15) and projected-augmented wave (PAW) method.[16] According to DFT theory, the ground state energy of a many electron system can calculate using a functional of the electron density. Therefore, the ground state energy of a system can be obtained by energy minimization with respect to the electron density. The PAW method increases the efficiency of computational time. The GGA was used with the exchange-correlation functional of Perdew and Wang (PW91).[17] The reason for using the GGA method is that it uses some recent theoretical studies which showed higher accuracy than other approximations such as the local density approximation to calculate various properties of bulk nickel[18] or to calculate the formation and migration enthalpies of vacancies in nickel.[19]

The plan-wave cut off energy was set as 400 eV for all calculations and $3 \times 3 \times 3 \times$ Monkhost-Pack[20] meshes were used to test the Brillouin zone in the reciprocal space, depending on the size of the studied unit cell. To determine the insertion energies of oxygen and vacancy formation energy in Ni, three different sizes ($2 \times 2 \times 2$, $3 \times 3 \times 3$, and $4 \times 4 \times 2$) of FCC (face-centered cubic) supercell having 32, 108, and 128 lattice sites were used to calculate the Ni and NiO bulk energy.

To simulate one of widely used Ni-base structural alloy, Alloy 600 which is mainly composed of 72% Ni and 15% Cr, a supercell containing 28 nickel atoms and 4 chromium atoms was modeled for the study of Ni-Cr binary alloy. Figure 1 shows the atomic structure of supercell used in this calculation. In order to determine the diffusivity of oxygen in nickel and Ni-Cr binary alloy, it was needed to calculate the activation energy, E_O^{act} for the possible diffusion path. For the saddle point corresponding to the migration of the atomic oxygen, the minimum energy path was determined by using the nudged elastic band (NEB) method of Henkelman *et al.*[21] NEB method is widely used to calculate the potential energy maximum along the minimum energy path. Five images were used for the NEB calculation per each diffusion path to calculate the activation energy of oxygen in pure Ni and Ni-Cr binary alloy.

Before every test step, lattice relaxation task was performed by using a conjugate-gradient (CG) algorithm for insertion energies and all ions were allowed to relax while the supercell volume was kept constant but could change shape. The charge transfer between oxygen, nickel, and chromium was determined with the algorithm of Henkelman *et al.*,[22] which carried out a Bader decomposition of the electronic charge density into atomic contributions.

To validate the results, some general parameters were calculated such as cohesive energy of Ni, insertion energy of oxygen in pure Ni, and vacancy formation energy. The cohesive energy of Ni is defined as total energy of the supercell divided by number of Ni atoms in the supercell. Table I shows the calculated cohesive energy of Ni as the supercell size increases. The calculated cohesive energy of Ni are 5.461 eV for $2 \times 2 \times 2$ and for $4 \times 4 \times 2$ supercell, and 5.462 eV for $3 \times 3 \times 3$ supercell, respectively. It is almost constant irrespective of the supercell size, which means that $2 \times 2 \times 2$ supercell is sufficient for further calculations.

TABLE I. Calculated cohesive energy of Ni (eV).

Supercell size	$2 \times 2 \times 2$	$3 \times 3 \times 3$	$4 \times 4 \times 2$
Cohesive energy	5.461	5.462	5.461

The vacancy formation energy E_{Ni}^{vac} is defined as

$$E_{Ni}^{vac} = E_{nNi} + E_{Ni}^{coh} - E_{(n-1)Ni}, \quad (1)$$

where E_{nNi} is the total energy of the supercell containing (n) atoms of Ni, E_{Ni}^{coh} is the cohesive energy of nickel, and $E_{(n-1)Ni}$ is the total energy of the supercell containing $(n-1)$ atoms of Ni. The vacancy formation energy of Ni was calculated to be 1.39 for $2 \times 2 \times 2$ supercell and 1.4 eV for $3 \times 3 \times 3$ supercell, respectively, and the results in this study are compatible with previous studies by Garruchet *et al.*[8] and references therein.

The insertion Energy E_O^{ins} is defined as

$$E_O^{ins} = E^{nNi} + E_O - E^{nNi+O}, \quad (2)$$

where E^{nNi} is the total energy of the supercell, E_O is the energy of the oxygen atom, and E^{nNi+O} is the total energy of the supercell containing (n) atoms of Ni and the O atom inserted in the Ni. The calculated insertion energy of oxygen in nickel is 3.39 eV for $2 \times 2 \times 2$ and 3.38 eV for $3 \times 3 \times 3$, respectively. Comparing to previous experimental data of oxygen insertion in nickel by Park and Altstetter's work,[23] the current model confirmed that the position of atoms and the calculation methods are correct.

As illustrated in Figure 2, there are two different diffusion pathways of oxygen in FCC metals and alloys. Oxygen atom can pass through an adjacent tetrahedral (T) site via a face of the octahedron (O), which is called after O-T-O pathway as represented as red arrows in Figure 2. Alternatively, oxygen atom can diffuse from one O site to adjacent O site

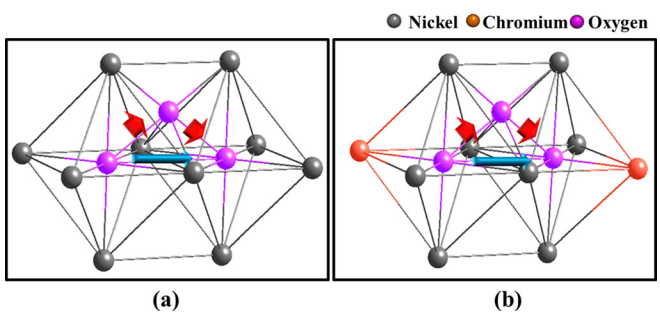

FIG. 2. (Color online) Diffusion pathway of atomic oxygen in (a) pure Ni, and (b) Ni-Cr binary alloy; Long horizontal arrows indicate O-O paths, and short tilted arrows O-T-O paths.

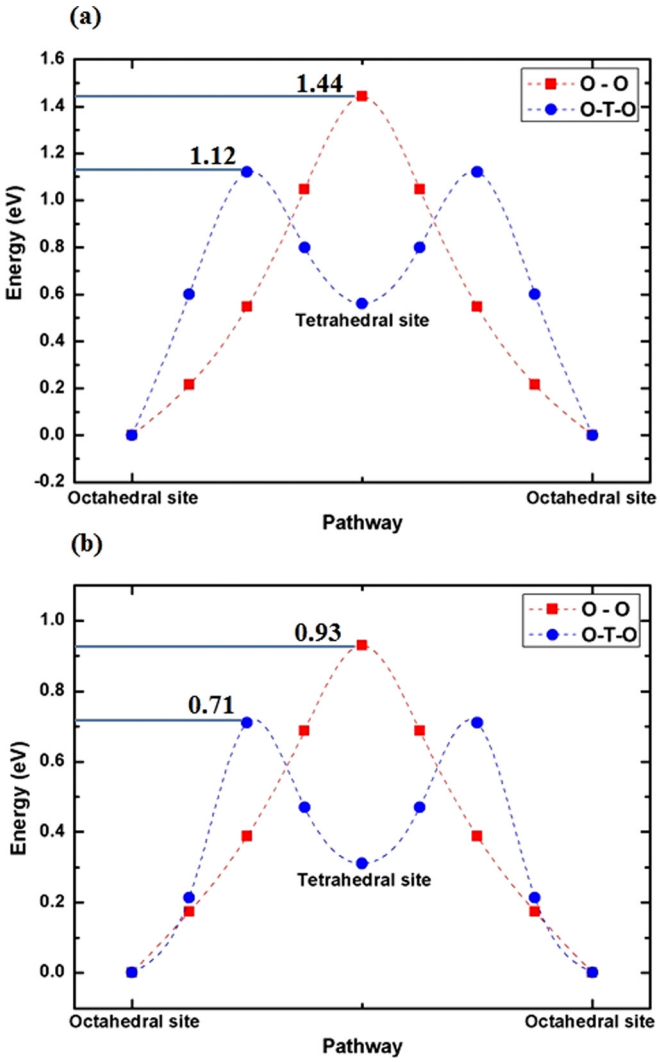

FIG. 3. (Color online) Energy of oxygen transport calculated by NEB method in (a) pure Ni, and (b) Ni-Cr binary alloy.

directly, which is called after O-O pathway as represented as blue arrow in Figure 2. The activation energy of oxygen diffusion was calculated by NEB method along the two different pathways including O-O and O-T-O. The calculations for two cases of oxygen diffusion were performed in pure Ni and Ni-Cr binary alloy, respectively.

The calculated activation energy for the diffusion of oxygen in pure nickel is 1.44 and 1.12 eV along the O-O and O-T-O diffusion pathway, respectively. Figure 3(a) shows the energy of oxygen transport calculated by NEB method in pure Ni along the two difference pathway and highest energy barrier is activation energy of oxygen diffusion in each pathway. The results show good consistency with Megchiche *et al.*'s work,[10] but a slight difference might be caused by the difference in number on the KPOINT grid. Megchiche *et al.* used $4 \times 4 \times 4$ and $6 \times 6 \times 6$ KPOINT, but $3 \times 3 \times 3$ KPOINT was used in this study. Using a small KPOINT increases the computational speed but also increases the chances of error. The calculated activation energy along the O-T-O pathway shows lower value than that along the O-O diffusion pathway in this study. This means that oxygen can easily diffuse along the O-T-O diffusion pathway comparing to the O-O pathway. Theoretically, in case of interstitial diffusion in FCC structure, the octahedral site is the most stable state and when the tetrahedral interstitial site is sufficiently deep, diffusing interstitial oxygen atom can be equilibrated at the metastable tetrahedral site temporarily and then jumps forward or backward to a neighboring octahedral site.[24] Therefore, the results in this study coincide well with theoretical expectation.

TABLE II. Calculated activation energy of oxygen diffusion in pure nickel and Ni-Cr binary alloy (eV).

32Ni + O		28Ni4Cr + O	
O-O	O-T-O	O–O	O-T-O
1.44	1.12	0.93	0.71

In the case of Ni-Cr binary alloy, the calculated activation energies for diffusion of oxygen are 0.93 eV and 0.71 eV along the O-O and the O-T-O diffusion pathway, respectively. Figure 3(b) shows the energy of oxygen transport calculated by NEB method in Ni-Cr binary alloy along the two difference pathway and highest energy barrier is activation energy of oxygen diffusion in each pathway. Table II shows the result of calculated activation energy for diffusion of oxygen in Ni-Cr binary alloy with comparison of the result in pure nickel. The activation energy along the O-T-O path is lower than that along the O-O pathway not only in pure Ni but also in Ni-Cr binary alloy. It shows that oxygen can easily diffuse along the O-T-O pathway even in Ni-Cr binary alloy. Comparing the activation energy of oxygen diffusion in pure nickel, the activation energy of oxygen diffusion in Ni-Cr binary alloy is lower than that in pure nickel. The diffusion coefficient is classically expressed in the form of Arrhenius plot as shown in the following equation:

$$\mathrm{D} = D_0 e^{-Q/kT}, \tag{3}$$

where D_0 is the temperature-independent pre-exponential factor, Q is the activation energy, and k is the Boltzmann constant. According to this equation, the lower activation energy means that the diffusion coefficient is higher. The diffusion coefficient is an important parameter for internal oxidation phenomena. Even Scott and Calvar[5] insisted that the crack growth rate can be obtained by the following equation without chemical reaction:

$$\mathrm{x} = \sqrt{2Dt}. \tag{4}$$

According to the activation energy results, chromium increases the oxygen diffusivity in Ni-Cr binary alloy, and it leads to an increase in the crack growth rate. Referring to Chattopadhyay and Wood's work,[25] however, the diffusion coefficients of oxygen are $2.4 \times 10^{-9}\mathrm{cm}^2/\mathrm{s}$ at 1000 °C and $1.74 \times 10^{-11}\mathrm{cm}^2/\mathrm{s}$ at 1000 °C in nickel and Ni-Cr (12 wt. %) binary alloy, respectively. And, according to experimental data by Vaillant *et al.*,[26] the increase of chromium contents in nickel base alloys tends to reduce the growth rate of environment-assisted crack by the formation of passive oxide film on its surface. The results tend to contradict the experimental data. However, when calculated with pure Cr, the activation energy of oxygen diffusion is estimated to be 0.2 eV.

Therefore, it seems to be consistent that the activation energy decreases when Cr is included in the calculation in this study. In the current model, oxygen can diffuse easier into the chromium matrix than into the nickel matrix because the chromium has smaller atomic radius than that of nickel, and forms a bcc (body-centered cubic) structure. It is agreement with lower activation energy in chromium than that in nickel. However, the current model based on the first principles calculation needs to consider the oxide formation and its effects on atomic diffusion. Although passivity or passive oxide formation is one of most important factors in the analysis of the diffusion phenomena in metals and alloys, it has not been adopted for the first principle calculational model so far. Therefore, the method will be further investigated in our research to calculate the oxide films formation or passivity of metal or alloys using first principles calculation.

This work was focused on the prediction of oxygen diffusion behavior in pure nickel and its extension to Ni-Cr binary alloy in order to understand the fundamental corrosion/oxidation behavior of nickel base structural alloys. The VSAP calculation package was used for the first-principles calculation. Key parameters including cohesive energy, insertion energy, and vacancy formation energy were calculated, and the results coincide well with experimental data and theoretical expectation.

From the calculation of the activation energies for diffusion of oxygen, the results showed that the activation energy for diffusion along the O-T-O path is lower than that along the O-O path in pure nickel as well as in Ni-Cr binary alloy, which implies that the oxygen can more easily diffuse along the O-T-O path than O-O path. Comparing to calculated activation energy for diffusion of oxygen in pure nickel, the activation energy for diffusion of oxygen in Ni-Cr binary alloy resulted in lower value, which contradicts the experimental data and previous observation. The deviation is believed to be originated from the fact that the current model based on the first principles calculation does not consider the oxide formation and its effects on atomic diffusion. Therefore, the method will be further investigated in our research to calculate the oxide films formation or passivity of metal or alloys using first principles.

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